Research Article

Synthesis of Nanomagnetite for Fertilizer Applications

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Abstract

A novel method for preparing nano magnetite and EDTA stabilised magnetite nanoparticles in large scale for fertilizer application is discussed. A co-precipitation method in aqueous medium using single iron (III) salt as a precursor is followed. A 2:1 mole ratio for Fe^{+3} and Fe^{+2} were achieved by reducing one third mole of initial iron (III) salt by potassium iodide (KI). Filtration of the iodine formed is followed by hydrolysation of filtrate using ammonia solution to a pH in the range of 9 - 11. Highly selective and stabilised nano material product with prominent yield indicates the method is environment friendly and green. Stabilization with EDTA helps to keep the nano particles in suspended form for seed priming or foliar application as a micronutrient source for plants.

Keywords: Nano Fertilizer, Nano magnetite, EDTA stabilization

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Introduction

Recent advances in nano technology have proved to be promising for many areas such as the Food sector, biomedicine, environmental engineering, safety and security, water resources, energy conservation [1, 2]. The importance of the sector of agriculture lies within the undeniable fact that it provides food and raw material for feed industry. With the expansion of population in world, development of agricultural produces ought to be a lot economical, viable, environmentally friendly and efficient. The importance of exploitation nanotechnology in agriculture includes specific application of nanoparticles through foliar spray as nanofertilizer or nanopesticide to extend the productivity while not harming soil and water, and protection against many microbial diseases. This technique may facilitate achieving sustainable growth of agriculture and enhance the nutrient uptake of the plant [3-5]. The application of nano-fertilizers can improve the absorption of phytonutrients through leaf or root pores. This process may create new pores or promote complexation with molecular transporters or root exudates using endocytosis or ion channels [6].

The importance of iron as a vital micronutrient for life is because of its essential role in metabolic processes such as DNA synthesis, respiration and photosynthesis in plant [7, 8]. Iron is involved in the synthesis of chlorophyll and is essential for the upkeep of chloroplast structure [9]. Preparation of oxides of iron in nano form is commonly found feasible with mainly three forms known as Nanoscaled Zero Valent Iron (nZVI), Maghemite nanoparticles (γ-Fe_2O_3) and Magnetite nanoparticles (Fe_3O_4, which exhibit magnetic properties) [10, 11]. Magnetic iron nanoparticles (Fe_3O_4) are synthesised by co-precipitation in aqueous solution by adding hydroxide in to iron salt solution. However, without proper stabilization, these particles tend to agglomerate to reduce the energy associated with increased surface area to volume ratio [12]. Further the nanoparticles are chemically terribly active and simply oxidised in air that usually shows low magnetic properties and dispersibility. Hence, stabilising the particles during synthesis itself for long term storage until application as plant nutrient is essential. This can be achieved by using surfactants, polymers or inorganic film (silicon, carbon) that forestall from oxidation and agglomeration. Recent studies show high affinity of EDTA towards iron nanoparticles, which can improve colloidal dispersibility, decrease high surface energy and additionally decrease agglomeration [13].

Present study gives information about synthesis and characterisation of nano Fe_3O_4 and EDTA stabilised nano magnetite (Fe_3O_4) using single iron (III) precursor [14] and preparation of its dispersion solution using suitable dispersing agents for applicability as fertilizer in agriculture [15].

Materials and Method

The chemicals and reagent used for preparation of EDTA stabilised Fe_3O_4 are anhydrous $FeCl_3$ (AR Grade), Potassium iodide (KI) (AR Grade), EDTA (AR grade) obtained from certified chemical manufacturers and are used as such. Surfactant used is Tersperse 2700, a product from Indorama Chemicals.

Both the nanoparticles - nanoFe_3O_4 and nanoFe_3O_4-EDTA (EDTA stabilised nano magnetite) - are synthesised in similar manner minor differences in work up procedure. $FeCl_3$ and KI aqueous solutions are mixed in a mole ratio of

3:1 and the iodine (I_2) formed due to reduction of $FeCl_3$ is filtered out. The filtrate is then hydrolyzed using ammonium hydroxide solution (24%). The black magnetite particles formed during hydrolysis is then filtered, washed with water and dried at 250°C to get nano-Fe_3O_4. For preparation of Fe_3O_4-EDTA 0.02N EDTA solution is added to the reaction material before hydrolysis and heated at 50°C for an hour before filtration. Precipitate is then washed with water and dried at 80°C in an oven for 3-4 hour.

The chemical reaction is:

$$3Fe^{+3}_{(aq)} + I^{-}_{(aq)} \rightarrow 2Fe^{+3}_{(aq)} + Fe^{+2}_{(aq)} + 1/2(I_2) \qquad (1)$$

Experiments are detailed below.

A. Nano-Fe_3O_4: Anhydrous $FeCl_3$ (21.02 g - 0.129 mol) is dissolved in DM water with stirring. KI (7.17g - 0.043 mol) is added to this solution pinch by pinch. After the addition, stirring is continued for an hour for completion of reaction. The Iodine (I_2) precipitated is filtered and washed with water and dried in a desiccator (5.05 g, 92.7% yield). The filtrate and washing solution are combined and hydrolysed with ammonia solution (24 % strength) up to PH 9-11 to precipitate magnetite nanoparticles. It is then left for settling of precipitate for about an hour and then filtered. The precipitate is washed with DM water and dried at 250°C. Yield of material is 89 % (8.9 g against targeted 10 g).
B. Nano-Fe_3O_4-EDTA: A sample of 21.02 g (0.129 mol) of anhydrous $FeCl_3$ is weighed and dissolved in DM water with stirring. To the solution, 7.17g (0.043 mol) of KI is added pinch by pinch continuing the stirring until completion of reaction. The precipitated Iodine(I_2) is filtered and washed and dried in a desiccator and weighed to get 92.9 % yield. The filtrate and wash was combined and hydrolysed using ammonia solution of 24 % strength to pH 9 - 11. Nano-magnetite precipitated is black in colour. EDTA solution of 0.02N strength is then added and heated the reaction mass for 1 hour at 50°C and allowed to settle. The precipitate is then filtered and washed with DM water and then dried in oven at 80°C for 3-4 hour. Final weight of the obtained product is 10.1 g, which is a 99 % yield.

The difference in the yield in the two cases may be attributed to the high activity of nanoparticles. Stabilization using EDTA leads to higher yield.

Characterisation of Nanoparticles

The average hydrodynamic particle size and the zeta-potential of the samples were determined by dynamic light scattering (DLS) using Zeta Sizer (ver 6.34) Nano ZS (Malvern). The mean diameter of particles Dm was determined from the average value of the light scattering intensity calculated by the program attached to the instrument. Measurements were performed at 25°C temperature. The presented values of the zeta potential represent averaged results of twelve individual measurements recorded for the same suspension. Zeta potential of nanoFe_3O_4 is -1.44 mV and for nanoFe_3O_4-EDTA is -16.2 mV, while when make it suspension with tersperse 2700 it gives result -28.3 mV, which indicate good stability. Measurements of the hydrodynamic size of nanoparticles by DLS method testify that particle size distribution in the aqueous suspension, with an average diameter of particles of 340 nm. Addition/adsorption of EDTA did not change the mode of size distribution, but gave a shift of the distribution curve to higher d values, and the average particle diameter increased to 1736 nm which is caused by coagulation, While when suspended in solution with surfactant like Tersperse 2700, particle size is 246 nm. Modal and average particles sizes of Nano particles are shown in **Table 1**. Smaller size of dispersed nano particles indicates towards its applicability as a foliar nutrient source in agriculture. The iron content is estimated by gravimetric method. Presence of EDTA is established by nitrogen estimation by Kjeldahl method. Magnetic property of nanoparticles is tested using a permanent magnet as shown in **Figure 1**.

Table 1 Particle size distribution obtained from DLS

Product name	Symbolic name	Model particle size(nm)	Average particle size(nm)
Magnetite Nano Particle	Nano Fe_3O_4	186.3	340
Stabilised Magnetite Nano Particle	Nano Fe_3O_4-EDTA	928.1	1736
Dispersed Magnetite Nano Particle	dispersed Nano Fe_3O_4-EDTA	164.9	246

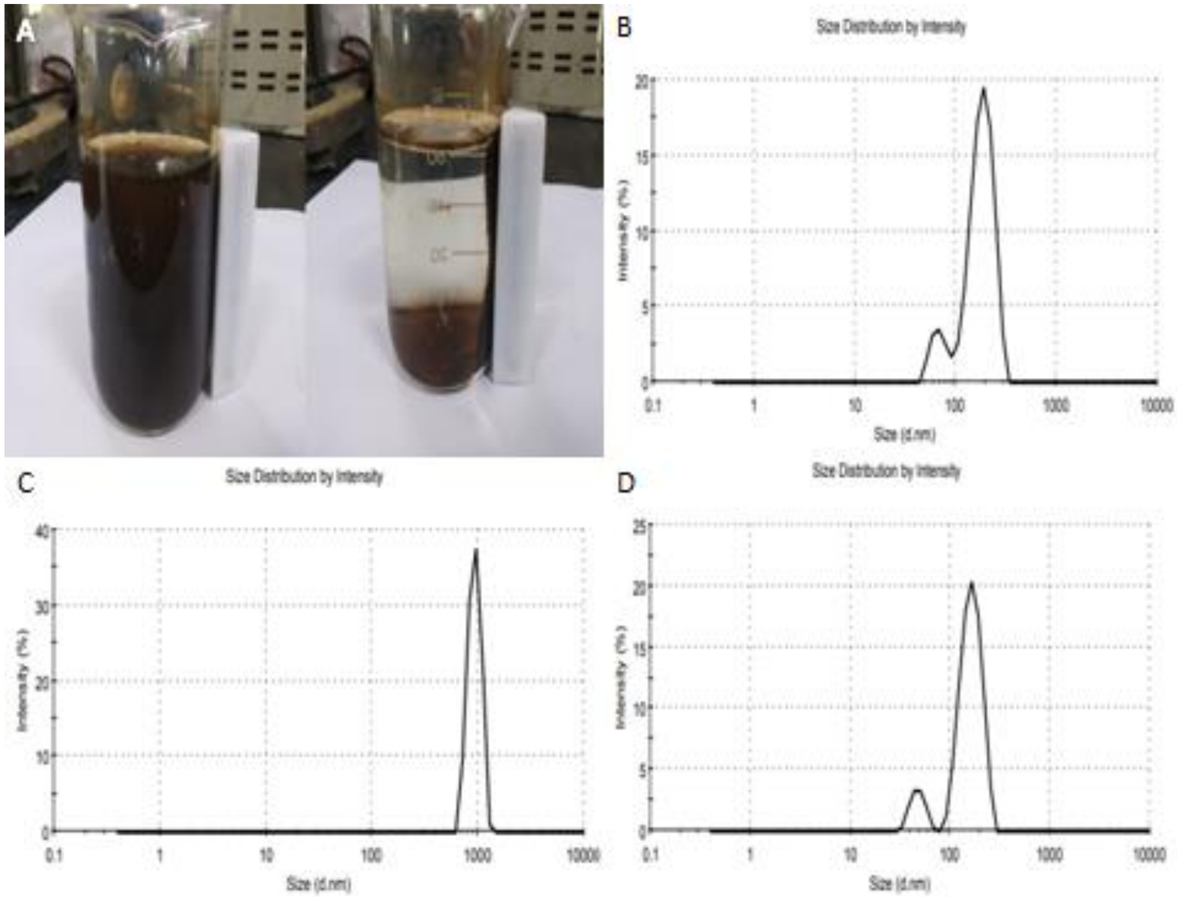

Figure 1 A- EDTA stabilised nano magnetite attracted by external magnet. 1B- Size distribution of magnetite nano particles. 1C- Size distribution of EDTA stabilised magnetite nano particles. 1D- Size distribution of dispersed EDTA stabilised magnetite nano particles with Tersperse 2700 surfactant

Discussion

The product nanoparticles are coloured black, and are strongly attracted towards a slab magnet. Instead of the known practice of using two different iron salts (Fe(III) and Fe(II)) as precursors for synthesis of nano – Fe, only single aqueous iron(III) salt solution is used in the new method. Reduction of the salt using potassium iodide is attained by maintain the appropriate mole ratio according to Equation (1). It is possible to synthesise 100g of stabilised magnetite nano particle in single experiment, reproducibly. Bulk production of the material for application as a micronutrient source is hence possible.

Suspension of both stabilised and non-stabilized magnetite nanoparticles form suspension with water but suspension of non-stabilized nano particle get coagulated and settle down within a 24 hour. This could be due to their chemically active behaviour to get oxidised. This will lead to the loss of magnetic property and dispersibility. EDTA - stabilised magnetite nano particles suspension in water remain stable more than 3-4 days. This could be due to the grafting of EDTA which prevent from oxidisation and agglomeration. Use of EDTA also supports the assimilation of nutrients by plants when applied as a fertilizer.

The method for the preparation of magnetite is economical and green, achieving a high selectivity and atom economy percents [16]. However to make it use as fertiliser it should make proper and long lasting dispersion. EDTA stabilised nano magnetite make excellent dispersion with many organic chemicals [17]. Although a suspension prepared using ethylene glycol as dispersing agent remains stable up to more than 80 days [18], but ethylene glycol being hazardous to plant, it inhibit the growth. The dispersing agent must be bio degradable and non toxic for soil. Out of the many dispersing agents tried (Tersperse 2700, sodium dodecylebenzene sulfonet (SDBS), Tersperse 2020, Carboxy methyl cellulose), the best result of stable suspension is obtained while using Tersperse 2700. When the solution is ultra-sonicated for 30 min, the suspension remains stable for up to 90 days. The results are indicative of a promising source of Fe micronutrient source for agriculture. The nanofertilizer prepared is applied to broccoli during a field study and obtained promising results [19]. Seed priming experiments conducted using the prepared nanofertilizer gave conclusive results [20].

Conclusion

Novel agricultural methods demands development of novel sources of micronutrients sources. A method for bulk preparation of nano Fe source for fertilizer application is developed. The surface physical and chemical environments of the magnetite nanoparticles are affected by the added EDTA due to the strong interaction between magnetite nanoparticles and EDTA, which leads to great stabilisation of highly reactive magnetite nanoparticles which supports it to remain in suspension form in water. The results reflect high homogeneity in nanoparticles shape and size of the samples studied. The addition of EDTA may also act as a barrier to the growth of nanoparticles nuclei, thus decreasing nanoparticles size. When it is dispersed in water using a long chain polymer surfactant Tersperse 2700 the nano particles of EDTA stabilised magnetite remain in suspension for a long time, which can be used as fertilizer in seed priming as well as foliar spray.

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